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Toward Thermoplastic Lignin Polymers; Part II: Thermal & Polymer Characteristics of Kraft Lignin & Derivatives

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This work focused on providing a molecular understanding of the way the polymeric properties of kraft lignin and its derivatives are affected by various thermal treatments. This information was then correlated with the polymeric properties of the materials (glass transition temperature (T_g), molecular weight characteristics, and thermal stability) for a series of selectively and progressively derivatized softwood kraft lignin samples. Softwood kraft lignin was highly susceptible to thermally induced reactions that caused its molecular characteristics to be severely altered with the concomitant formation of irreversible cross-linking. However, by fully methylating the phenolic OH groups from within the structure of softwood kraft lignin, the thermal stability of these materials was dramatically enhanced and their T_g reduced. While optimum thermal stability and melt re-cycling was observed with the fully methylated derivatives, fully oxypropylated phenolic substitution did not offer the same possibilities. The accumulated data is aimed at providing the foundations for a rational design of single component, lignin-based thermoplastic materials with reproducible polymeric properties when thermally processed in a number of manufacturing cycles.
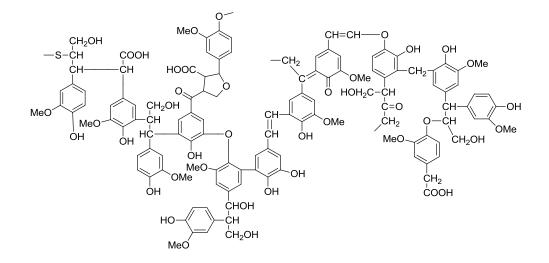
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INTRODUCTION

As a natural and renewable biopolymer, lignin is next only to cellulose in natural abundance, since it is an integral part of the plant cell wall. Native lignins are created via enzyme-mediated processes involving three primary hydroxycinnamyl alcohol precursors (monolignols), *i.e.*, p-coumaryl alcohol, coniferyl alcohol, and synapyl alcohol, which lead to p-hydroxylphenylpropane (H), guaiacyl (G), and syringyl (S) structural units being incorporated into their complex structure (Boerjan *et al.* 2003; Bonawitz 2010). Generally described as rather uniform, a typical softwood lignin consists of >95% G units (Gosselink *et al.* 2004), a minor amount of H units, and a trace amount of S units. Hardwood lignins, however, are composed of a mixture of predominantly G and S units with a small amount of H units (Fengel and Wegener 1984).

During the lignification process, the most abundant set of linkages created are those of aryl alkyl ethers (β-O-4), which account for more than 40% of the total linkages within softwood lignins, and up to 60% in hardwood lignins (Crestini *et al.* 2011; Sette *et al.* 2011). It is these ether linkages that are most susceptible to cleavage by technical kraft processes, which impart a large amount of phenolic hydroxyl groups within the structure of kraft lignins (Gierer 1980). The complex kraft delignification reactions also lead to

(amongst others) enol ethers and stilbenes linkages. A statistical scheme for softwood kraft lignin is shown in Scheme 1 as proposed by Marton (1971).

Scheme 1. A statistical structure of softwood kraft lignin that shows the large abundance of phenolic OH groups (Marton 1971)

Kraft lignins represent a major byproduct of the pulp and paper industry, since an enormous amount of such material is produced annually. The kraft wood pulping process accounts for nearly 85% of the total chemical wood pulp production (56 million tons in 2006) in the United States (Kramer *et al.* 2010).

Considering their aromatic, polymeric, renewable, and vast supply, such lignin sources undoubtedly represent significant commercial opportunities. They have long been viewed as a sustainable feed stock for chemicals (Bozell *et al.* 2007), a possible carbon fiber source (Amen-Chen *et al.* 2001; Kadla *et al.* 2002; Mathers 2012; Roberts *et al.* 2011), and potential biopolymer engineering materials (Doherty *et al.* 2011). Technical kraft lignins offer enhanced reactivity via their abundant phenolic OH groups with tangible possibilities for their utilization in adhesive and thermoset applications. For example, kraft lignin has been reported to replace up to 50% of the total amount of phenol required in phenol formaldehyde resins used in the production of plywood (Danielson and Simonson 1998). However, there are no reports of kraft lignin being used in single-component thermoplastics due to thermal stability considerations. So far, research efforts using milder thermal processing for technical lignin have centered on blending it with other synthetic polymers. For example, poly(ethylene oxide) was mechanically blended with hardwood kraft lignin to improve its extrusion processing characteristics prior to carbon fiber preparation (Kadla and Kubo 2003; Kadla *et al.* 2002; Kubo and Kadla 2005). Solution blending industrial softwood kraft lignin with poly(vinyl acetate) in the presence of plasticizers has shown to yield homogeneous thermoplastic, with T_g as low as 30 °C (Li *et al.* 1997; Li and Sarkanen 1999). A number of research efforts have also emerged aiming at lignin oxypropylation, which resulted in low T_g poly(propylene oxide) grafted lignin under the specified conditions, thus increasing the processing possibilities of lignin (Jain and Glasser 1993; Nadji *et al.* 2005; Wu and Glasser 1984). Furthermore, the poly(propylene oxide) grafted lignins were blended with ethylene-vinyl acetate copolymers for injection molding processes (Glasser *et al.* 1988).

Without modification, the decomposition of softwood kraft lignin has been reported to start at temperatures as low as 120 °C, indicated by the formation of formaldehyde (Fenner and Lephardt 1981). This effect can be explained by the elimination of primary γ methylol (CH_2-OH) groups from quinone methide intermediates, which are presumably derived from the minor residual β-O-4 linkages known to survive the kraft processes (Froass *et al.* 1996; Jiang and Argyropoulos 1999; Jiang and Argyropoulos 1994; Liitiä *et al.* 2003). The quinone methide intermediates involved in bulk kraft lignin can be formed via thermally inducing phenolic radicals, due to the fact that the O-H bonds in phenolic OH groups are of relatively low bond dissociation energies (Chandra and Uchimaru 2002). In addition, thermally and mechanically generated free radicals are known to exist within lignin (Rex 1960; Sazanov and Gribanov 2010). Such species are preserved within it by steric factors (cage effects) and have been measured by ESR to amount to as high as 3×10^{17} per gram of softwood kraft pulp (Steelink 1966). The steric hindrance of the long-lived radicals can be alleviated once the glassy state of lignin is converted into the rubbery state above its T_g. Therefore, when heated to high temperatures around T_g, long-lived radicals within technical lignin may facilitate the thermal generation of phenolic radicals.

If kraft lignins are to be thermally processed around their T_g, thermal stability considerations have to be taken into account (Jain and Glasser 1993; Nadji *et al.* 2005; Wu and Glasser 1984). In this respect, our recent work was focused on developing and optimizing the selective and facile masking of phenolic hydroxyls in technical lignin with the aim of reducing (and by extension modulating) its chemical reactivity and thermal stability (Sadeghifar *et al.* 2012).

Overall, our review of the literature has revealed that the molecular events that occur within technical lignin at low temperatures prevent it from being processed as a thermoplastic polymer. Such molecular events undoubtedly define vital polymeric properties of the material, including its T_g, molecular weight distribution, and thermal stability. Consequently, this work focused on a molecular understanding of the way the thermal properties of kraft lignin are affected by different chemical derivatizations. The conclusions from the accumulated data may provide the foundations for a novel rational design of single-component, kraft lignin-based, thermoplastic materials with consistent thermal properties when thermally processed in a number of heating and cooling manufacturing cycles (Argyropoulos 2012).

EXPERIMENTAL

Materials

Commercially available (Mead Westvaco) softwood kraft lignin (Indulin) was used in this work. Quantitative ^{31}P NMR analyses (Argyropoulos 1994, 1995; Granata and Argyropoulos 1995) on this material showed that the amounts of condensed, non-condensed phenolic, and aliphatic hydroxyl groups were 1.6, 2.2, and 2.4 mmol/g, respectively. The values M_w = 7,800 g/mol, M_n = 1,900 g/mol, and PDI = 4.1 were determined using gel permeation chromatography for the original underivatized kraft lignin sample. All chemicals and reagents used in this study were purchased from Sigma-Aldrich and Fisher Chemical companies and used as received.

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Methylation

For methylation, 1.0 g of softwood kraft lignin was dissolved in 15 mL of aqueous 0.7 M NaOH at room temperature. Appropriate amounts, ranging from 0.25 to 2.5 mmol of dimethyl sulfate (DMS) per each mmol of total phenolic OHs, were added and the solution was stirred for 30 minutes at room temperature. The mixture was subsequently heated at 75 °C for 2 hours. When high degrees of methylation were required, special care was taken to maintain reaction homogeneity by adding sodium hydroxide solution. After the reaction, the mixture was acidified (pH = 2.5) with 2 M HCl, and the solid precipitate was washed with excess deionized water and freeze-dried. GPC data: M_n = 1,900 g/mol, M_w = 7,900 g/mol, PDI = 4.2.

This methylation procedure has been found to be selective towards phenolic OH groups (Sadeghifar *et al.* 2012). The methylation level can be adjusted by varying the addition of DMS. When using 2.5 mmol of DMS per each mmol of total phenolic OH, this reaction nearly approached completion (>99%). For this work, such extensively methylated (>99%) kraft lignin samples are called "fully methylated kraft lignin."

Oxypropylation

Appropriate amounts of propylene oxide (as per the desired degree of functionalization (Sadeghifar *et al.* 2012) were reacted with the lignin solution in 0.5 M aqueous NaOH (10 mL/g of lignin) at 40 °C for 18 h. Finally, the mixture was acidified (pH = 2.5) with 2 M HCl and the solid precipitate was washed with deionized water and freeze-dried. GPC data: M_n = 2,000 g/mol, M_w = 9,100 g/mol, PDI = 4.6.

The oxypropylation procedure has also been found to be selective towards phenolic OH groups (Sadeghifar *et al.* 2012). The oxypropylation level can also be progressively increased. It nearly approached completion (>99%) using 2.5 mmol of propylene oxide per each mmol of total phenolic OH. For such extensively oxypropylated lignin samples, ^{1}H NMR analysis showed that, on average, less than two propylene oxide repeating units were grafted onto each phenolic OH group. This indicates the coexistence of multi-oxypropylated and mono-oxypropylated phenolic derivatizations in this work, when the former was largely suppressed by milder reaction conditions (Sadeghifar *et al.* 2012). For this work, the extensively oxypropylated (>99%) kraft lignin samples are referred to as "fully oxypropylated kraft lignin."

Quantitative ^{31}P NMR

The degrees of methylation and oxypropylation of the softwood kraft lignin were determined using quantitative ^{31}P NMR, following published procedures (Argyropoulos 1994, 1995; Granata and Argyropoulos 1995). The methodology was also used to detect variations of the OH-bearing functional groups as they occurred during thermal treatments of lignin samples, providing valuable chemical evidence pertaining to the thermal stability studies carried out. An accurately known amount of 40-45 mg of dried lignin sample was weighted and dissolved in 500 μL of an anhydrous pyridine/CDCl$_3$ mixture (1.6:1, v/v). Two hundred μL of endo-N-hydroxy-5-norbornene-2,3-dicarboximide (e-NHI) solution (9.23 mg/mL as the internal standard and 50 μL of chromium (III) acetylacetonate solution (5.6 mg/mL) in the above pyridine/ CDCl$_3$ solution) as a relaxation reagent were then added. Finally, 100 μL of phosphitylating reagent (2-chloro-4,4,5,5-tetramethyl-1,2,3-dioxaphospholane, TMDP) was added prior

to NMR acquisition. NMR spectra were acquired using a Bruker 300 MHz spectrometer equipped with a Quad probe dedicated to ^{31}P, ^{13}C, ^{19}F, and ^{1}H acquisition.

Acetobromination

Due to the variable solubility that lignin samples display in THF, all samples examined in this work were subjected to a fast room temperature derivatization procedure, the feasibility and reliability of which has been examined in our laboratory (Asikkala *et al.* 2012). Five mg of a dried lignin sample were mixed in 2 mL of a glacial acetic acid/acetyl bromide mixture (92:8, v/v). The reaction mixture was stirred at room temperature for 2 hours. Finally, the solvents were completely removed at room temperature using a rotary evaporator connected to a cold trap-protected vacuum pump.

Gel Permeation Chromatography (GPC)

GPC measurements were carried out using a Waters GPC instrument, equipped with UV and RI detectors using THF as the eluent at a flow rate of 0.6 mL/min at 35 °C. Two ultrastyragel linear columns linked in series (Styragel HR 1 and Styragel HR 5E) were used. A series of monodispersed polystyrene standards were used for calibration.

Differential Scanning Calorimetry (DSC)

All glass transition temperature analyses were performed on a TA Instrument, model TA-Q100, in a temperature range of 30 to 200 °C. All samples were dried at 60 °C for 12 h in a vacuum oven prior to the DSC analysis. Approximately 5 mg of a sample were weighed directly in a DSC aluminum sample pan, which was then sealed by the lid of a pinhole by cold-pressing. An annealing procedure at a temperature lower than the sample's T_g was developed and optimized, *i.e.*, after loading into the TA-Q100, all samples were heated at 105 °C at a rate of 5 °C/min and then isothermally conditioned for 40 minutes prior to being quenched to 30 °C. Eventually, the DSC thermograms were recorded by increasing the temperature to 200 °C at a rate of 10 °C/min.

Thermal Gravimetric Analysis (TGA)

All TGAs and designed thermal treatments were carried out on a TA Instrument (TGA-Q500) using a nitrogen flow at a rate of 60 mL/min. For TGA studies, the sample size was approximately 15 mg. All samples were initially heated to 105 °C (heating rate of 10 °C/min) and kept isothermally for 20 minutes before being heated to 600 °C at a heating rate of 10 °C/min.

Thermal Stability Studies

For comparison, the thermal stability of the original kraft lignin and its fully derivatized counterparts were examined using a TGA-Q500 instrument. Each kraft lignin sample was placed within the furnace of the TGA-Q500 instrument using a nitrogen flow rate of 60 mL/min. The temperature was then increased (heating rate = 10 °C/min) to 20 °C above its T_g and kept isothermally for selected time intervals. The furnace was then cooled to 40 °C at a rate of 10 °C/min. The treated samples were subsequently subjected to molecular weight characterization, T_g determination, and hydroxyl content analysis using GPC (after acetobromination), DSC, and quantitative ^{31}P NMR analyses, respectively.

To simulate real processing conditions, about 60 mg of the fully methylated kraft lignin sample was placed within the furnace of the TGA-Q500 instrument using a nitrogen flow rate of 60 mL/min and subjected to a three-cycle thermal treatment by heating it at a temperature 20 °C above the T_g for 60 minutes and then cooling it to room temperature. After each cycle of thermal treatment, a small portion of sample was taken for GPC analysis.

RESULTS AND DISCUSSION

Glass Transition Temperature

Once a polymer is subjected to a differential scanning calorimetric (DSC) scan (Hatakeyama and Hatakeyama 2010; O'Neill 1964), an endothermic enthalpy relaxation process (Hodge 1994; Petrie 1972) usually occurs that may affect the T_g determination measurement. For this reason, it is often recommended that the sample be subjected to an initial scan (above its T_g) to eliminate the stored thermal history within the polymer's glassy state (Rials and Glasser 1984). The highly amorphous nature of kraft lignin coupled with its complex hydrogen bonding interactions can induce significant enthalpy relaxation. This was manifested as a broad endothermic peak covering and extending beyond its glassy region during the initial DSC scan of the original underivatized kraft lignin (Fig. 1A). To overcome such a strong enthalpy relaxation and for the purpose of an accurate T_g determination, annealing all lignin samples above their T_g seems to be required (Rials and Glasser 1984). However, as previously mentioned, potential radical coupling reactions may be activated at temperatures around T_g that can introduce irreversible changes in the T_g values. For these reasons, at the onset of this work, an understanding of the way an initial thermal scan of the original underivatized kraft lignin at different temperatures affects its molecular weight was developed.

The original underivatized kraft lignin was thus subjected to different temperatures (120 °C, 130 °C, and 140 °C) under a nitrogen atmosphere within the furnace of the TGA-Q500 instrument for 30 minutes, followed by GPC analyses after cooling the treated samples to room temperature (Fig. 1B). Heat treatments of original kraft lignin samples at 130 ℃ and 140 ℃ apparently gave rise to high molecular weight tailing in each GPC profile; the M_w was found to be increased to 128,000 g/mol (a 16-fold increase) and 342,000 g/mol (a 44-fold increase), respectively. The higher molecular weight species produced were distributed over a broad molecular weight range, displaying no apparent modality in the chromatogram. This is not unusual in the context of molecular weight changes occurring within branched polymeric systems (Argyropoulos *et al.* 1987a,b,c). Cross-coupling of branched and highly functional molecular species typically leads to extensive polydispersity, as manifested in the tailing along the high molecular weight end of the chromatograms. This has been experimentally demonstrated (Argyropoulos *et al.* 1987a,c) and theoretically modeled with synthetic polymer systems (Argyropoulos *et al.* 1987b). In contrast, the molecular weight distributions of the samples heated at 120 °C showed negligible changes, except for some modality changes likely caused by the partial elimination of associated species as described in the literature (Contreras *et al.* 2008; Guerra *et al.* 2007; Sarkanen *et al.* 1982, 1984).
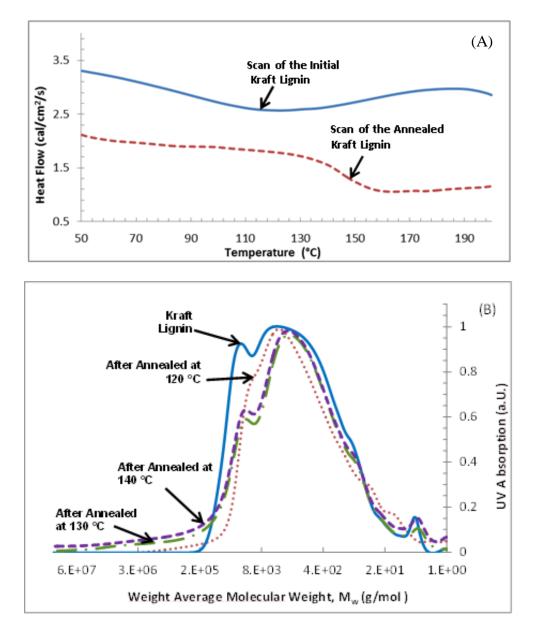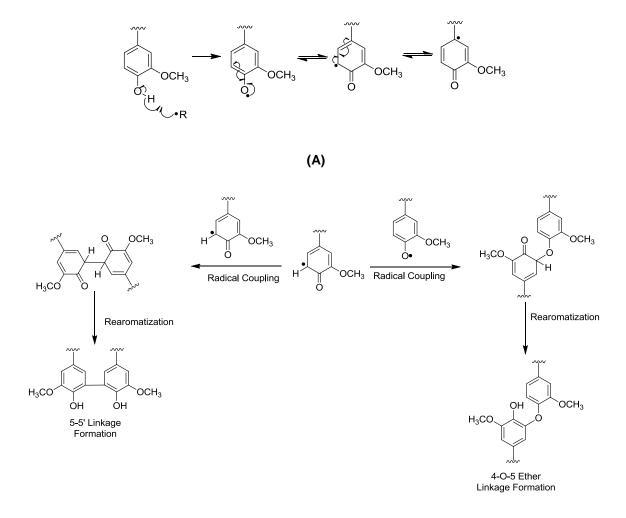
Fig. 1. Effect of heating on the molecular weight distribution of original underivatized softwood kraft lignin. Heating at 130 °C and 140 °C increases the molecular weight significantly by developing a broad tailing in the higher molecular weight region, while heating at 120 °C does not show significant changes.

It was thus concluded that for the purpose of suppressing the enthalpy relaxation for an accurate T_g determination for the original kraft lignin samples, any heating temperature above 120 °C should be precluded. Considering that 120 °C was also reported to be the degradation temperature of lignin (Fenner and Lephardt 1981), 105 °C was selected and used as a common annealing temperature for the other lignin samples in this work. The annealing procedure described in the experimental section has shown excellent effectiveness in the DSC analysis of the original kraft lignin sample when a distinct glass transition for the annealed sample is apparent (Fig. 1A).

Radical Coupling Mechanism of Kraft Lignin

The literature is abundant with fundamental studies aimed at deciphering the lignin fragmentation chemistry occurring at pyrolytic temperature regimes exceeding 200 °C (Antal 1985; Brebu and Vasile 2010; Evans *et al.* 1986). The early work of Fenner and Lephardt examined and profiled the evolved gases from the thermal decomposition of kraft pine lignin using Fourier transform infrared analysis (Fenner and Lephardt 1981). The authors reported the detection of formaldehyde at temperatures as low as 120 °C. Other studies carried out with lignin model compounds have also addressed such chemistry at relatively low temperatures (Kawamoto *et al.* 2007a,b, 2008a,b; Nakamura *et al.* 2007; Ohashi *et al.* 2011). Most of them report that radical pathways account for the observed transformations.

By using the accumulated literature knowledge, an attempt is made here to explain the data related to the thermal events observed in Fig. 1B and throughout this work (Schemes 2 & 3).
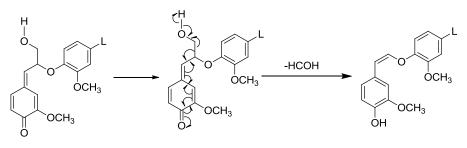

(A)

(B)

Scheme 2. Thermally induced events possibly occurring within softwood kraft lignin operating via radical mechanisms at low temperatures. (Gierer 1980; Gierer and Pettersson 1977; Kawamoto *et al.* 2007a; Kawamoto *et al.* 2007b; Kawamoto *et al.* 2008a; Kawamoto *et al.* 2008b; Nakamura *et al.* 2007; Ohashi *et al.* 2011)

At relatively low temperatures, radicals stabilized and trapped by steric factors within the solid structure of lignin (Sazanov and Gribanov 2010) may be activated (Scheme 2A). Phenoxy radicals can be generated via an H abstraction process when interacting with the thermally activated radicals (•R). The phenoxy radicals thus formed will readily transform into their various resonance mesomeric forms (Scheme 2A), eventually causing radical coupling reactions. For instance, either phenoxy radicals or their corresponding C_5-centered mesomeric radical derivatives can couple with C_5-centered radicals to form new 4-O-5 and 5-5'linkages, respectively (Scheme 2B).
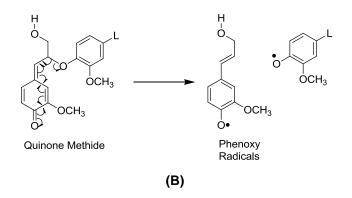
Since β-O-4 linkages have been reported to survive the kraft pulping process (Froass *et al.* 1996; Jiang and Argyropoulos 1999; Jiang and Argyropoulos 1994; Liitiä *et al.* 2003), the reported formation of formaldehyde at relatively low temperatures (Fenner and Lephardt 1981) can be explained by γ elimination of methylol (CH_2-OH) groups within residual β-O-4 linkages in kraft lignin (Scheme 3A) (Gierer 1980; Gierer and Pettersson 1977) via quinone methide intermediates, which are readily formed from the phenoxy radicals derived from the phenolic OH groups.

Quinone Methide   Formaldehyde Generation

(A)

Quinone Methide   Phenoxy Radicals

(B)

Scheme 3. Reactivity of the quinone methide intermediate and its contribution to radical pathways operating within lignin heated under 120 ºC. (Kawamoto *et al.* 2008a; Kawamoto and Saka 2007)

In addition to the elimination of the γ methylol (CH_2-OH) group of the β-O-4 linkage creating a stable enol ether (Scheme 3A) (Gierer 1980; Gierer and Pettersson 1977; Kawamoto and Saka 2007), homolytic $C_β$-O bond scission is a competing reaction pathway, responsible for the formation of two new phenoxy radicals (Scheme 3B)

(Nakamura *et al.* 2007). Derived from phenoxy radicals, the quinone methide intermediate can also undergo a re-aromatization process through a series of resonance-stabilized radical mesomers (Schemes 3A and 3B) (Kawamoto *et al.* 2007a,b). All these radicals transformed from the phenoxy radicals at lower temperatures than the T_g of the original kraft lignin are therefore assumed to induce radical coupling reactions leading to the observed molecular changes (Fig. 1B).

It is also worth noting that the radical coupling reactions within viscous kraft lignin media at low temperatures are more significant than dissociation reactions encountered under pyrolysis conditions requiring higher temperatures and heating rates (Brebu and Vasile 2010).

Effect of Heating on the Molecular Weight Characteristics of the Original Underivatized and the Fully Derivatized Kraft Lignin

Since the primary objective in this effort is the accumulation of data aimed at a rational design of lignin-based thermoplastics, the thermal instability of softwood kraft lignin at temperatures even below its T_g (153 °C) (Fig. 1B) represents a major obstacle that needs to be overcome. For lignin thermoplastic creation, stable melt characteristics are required when thermally processed above its T_g over a number of manufacturing cycles. Furthermore, the proposed radical mechanisms point to the need of derivatization chemistries for kraft lignin to inhibit the onset of radical coupling reactions. Additional experiments were, therefore, performed to offer a molecular understanding of the way the polymer properties of kraft lignin and its derivatives are affected as a function of their thermal treatment.

Since thermoplastic materials are always processed above their T_g, the original softwood kraft lignin and two fully derivatized (oxypropylated and methylated) samples were subjected to heating 20 °C above their T_g as a function of time. The treated samples were then subjected to molecular weight characterization using GPC. It should be noted here that the derivatization protocols applied were specific to the phenolic OH groups of the softwood kraft lignin (Sadeghifar *et al.* 2012), allowing for meaningful correlations to be made as to their role in defining thermal stability of kraft lignin and its derivatives.

Figure 2 shows that when the original underivatized softwood kraft lignin was heated under nitrogen at 173 °C (T_g = 153 °C) for only 20 minutes, its M_w increased and eventually exceeded 543,000 g/mol from 7,800 g/mol, a 70-fold increase. This increase is much more than those recorded when it was subjected to temperatures below its T_g, *i.e.*, 130 °C and 140 °C for 30 minutes (Fig. 1B). The same material eventually became highly cross-linked when heated for 30 minutes at 173 °C and could no longer be solubilized in THF, even after acetobromination. This can be explained on the basis of more radicals being activated at a temperature above T_g and the radical coupling reaction rates being significantly increased due to the reduced viscosity of kraft lignin.

For comparison, a fully ($\approx$ 99%) oxypropylated lignin (Sadeghifar *et al.* 2012) was heated to 148 °C, which is 20 °C above its T_g (T_g = 128 °C) (Fig. 2). There was a gradual increase observed in its M_w, which increased to 212,000 g/mol from 9,100 g/mol (23-fold increase) after 60 minutes of heating at 148 °C (20 °C above its T_g). Such thermal instability issues, therefore, represent a major limitation in processing this derivative as a thermoplastic.
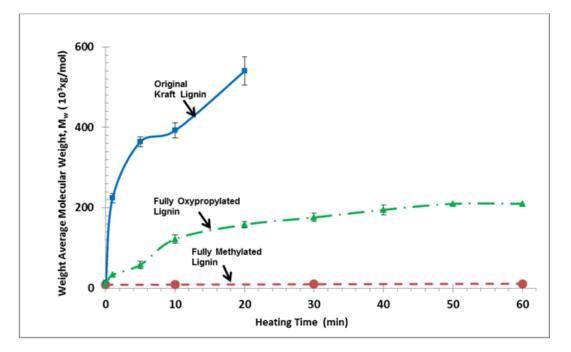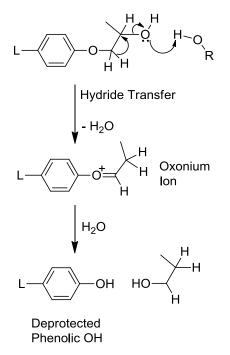
Fig. 2. Effect of heating on the molecular weight of the original underivatized and fully derivatized lignins. Dramatic increase in M_w is obvious in the original underivatized lignin while derivatized lignins show a smaller effect (oxypropylated) or no effect (methylated).

The thermal degeneration observed in the oxypropylated kraft lignin is possibly due to the dehydration of the secondary hydroxyl group of the oxypropyl substituent. For mono-oxypropylated phenolic OH components, their dehydration can be a facile reaction caused by an α-hydride transfer, eventually forming a phenoxonium intermediate (George and Prakash 2004; Vollhardt and Schore 2007) so that a new phenolic OH group can be generated by hydrolysis of the cationic intermediate, as depicted in Scheme 4. The newly formed phenolic OH groups will be further thermally activated and, to some extent, trigger radical coupling reactions resulting in further molecular weight increases in a manner similar to the original kraft lignin. The molecular weight increase of this derivative eventually leveled off after being heated for 50 minutes at 20 °C above its T_g (Fig. 2).

In an effort to validate the hypothesis depicted in Scheme 4, the following thermal treatment on fully oxypropylated kraft lignin was carried out. A 60 mg sample of fully oxypropylated kraft lignin was heated at 130 ℃ within the furnace of the TGA-Q500 instrument using a nitrogen flow rate of 60 mL/min for 30 minutes. Quantitative ^{31}P NMR analysis was subsequently used to determine the variations of its different hydroxyl group contents. As a result, 0.5 mmol/g of phenolic-OH groups were found to be generated, while 0.6 mmol/g of aliphatic-OH groups were eliminated. As per the suggestions of the reaction Scheme 4, new phenolic-OH groups are thus seen to be generated. They are most likely arising from the mono-oxypropyl masked phenolic-OH groups since their concomitant reduction is evident in the above measurements. The emerging new phenolic-OH groups can inevitably induce more radical coupling reactions as described for the unprotected original kraft lignin.

Scheme 4. A proposed mechanism for the thermal degeneration of the oxypropylated phenolic hydroxyl group. (George and Prakash 2004; Vollhardt and Schore 2007)
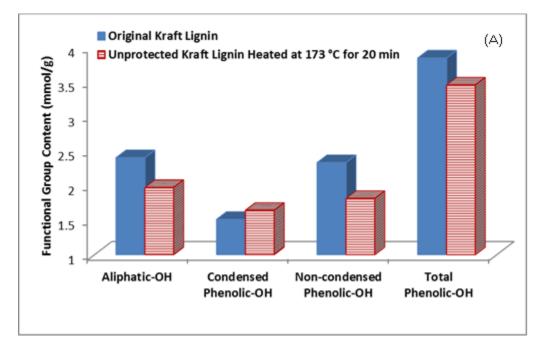
When the phenolic OH groups of softwood kraft lignin were fully methylated (> 99%) with dimethyl sulfate (Sadeghifar *et al.* 2012), a remarkable thermal stability of this derivative was apparent upon heating it at 148 °C (20 °C above its T_g) as a function of time (Fig. 2).
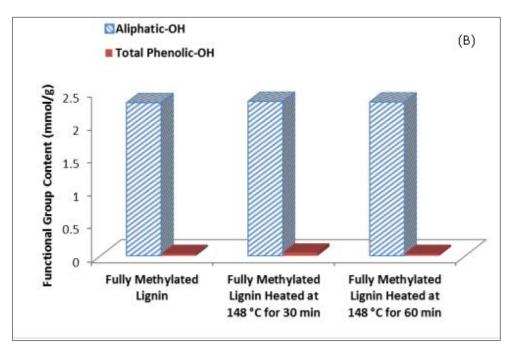
There was practically no observed molecular weight (M_w) increase within the fully methylated lignin when heated for 60 minutes at this temperature. The methylation of the phenolic OH groups of lignin is therefore a feasible derivatization method that enables kraft lignin to be used as thermoplastics. Apparently, the phenoxy radical formation, caused by H abstraction of the phenolic OH groups in kraft lignin, has been avoided by methylation-preventing, thermally induced, radical coupling reactions.
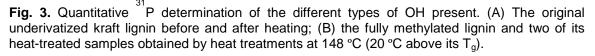
Thermally Induced Reactions in Kraft Lignin and Its Derivatives

In addition to the molecular weight characteristics, already charted as a function of thermal treatment using GPC, detailed analyses of the various hydroxyl-bearing functional groups present in initial and thermally treated kraft lignins and their derivatives can be carried out using quantitative ^{31}P NMR in the presence of an internal standard (Argyropoulos 1994, 1995).

Such quantitative data can offer additional informative insights into the actual thermal mechanisms involved. As such, the original underivatized kraft lignin and its fully methylated derivative (Sadeghifar *et al.* 2012) were subjected to quantitative ^{31}P NMR.

Fig. 3. Quantitative ^{31}P determination of the different types of OH present. (A) The original underivatized kraft lignin before and after heating; (B) the fully methylated lignin and two of its heat-treated samples obtained by heat treatments at 148 ºC (20 ºC above its T_g).

To understand and simulate thermal processing conditions, the original kraft lignin was heated at 20 °C above its corresponding T_g, *i.e.*, at 173 °C (for 20 minutes). For comparison, its fully methylated derivative was also heated at 148 °C (for 60 minutes) followed by quantitative ^{31}P NMR analyses. The ^{31}P NMR data shown in Fig. 3A, referring to the thermally treated original underivatized kraft lignin, indicates that the amounts of aliphatic and non-condensed phenolic hydroxyl groups were reduced by 18%

and 23%, respectively, while the amounts of condensed phenolic hydroxyl groups increased by 9%. These data are in agreement with the postulation that thermally induced radical coupling reactions involve phenolic OH groups. Radicals derived from the phenolic OH groups are prone to participate in coupling chemistry, creating condensed phenolic OH moieties such as 5-5' and 4-O-5 (Scheme 2B). Furthermore, the reduction of aliphatic OH groups can also be correlated to the thermal dissociation of an α-OH, creating a quinone methide intermediate and further γ methylol (CH_2-OH) elimination to form formaldehyde (Fenner and Lephardt 1981) and a new enol ether functionality (Schemes 3A, 3C, and 3D) (Domburg *et al.* 1974 ; Kawamoto and Saka 2007).

In addition to these rather dramatic thermally induced structural changes occurring within the original underivatized kraft lignin, the quantitative ^{31}P NMR data for the thermally treated fully methylated lignin (Fig. 3B) is also very revealing. However, this time practically no apparent changes occurred before and after the thermal treatment. The full derivatization (>99%) of the phenolic OH groups seems to prevent the formation of phenoxy radicals, even after 60 minutes heating at 20 °C above the T_g of the material.

To further understand the behavior of the original and derivatized kraft lignins and to shed more light into the various thermal degradation and crosslinking events, thermogravimetric analyses (TGA) were carried out (Table 1). $T_{1\%}$ (The specific temperature for a 1% weight loss) for the original underivatized kraft lignin sample was observed at 176 °C, whereas this temperature increased by 15 °C and 32 °C (191 °C and 208 °C) for the fully oxypropylated and methylated kraft lignin, respectively. It is interesting to see that beyond 2% weight loss, the thermal degradation temperatures ($T_{2\%}$ and $T_{5\%}$) of the fully methylated kraft lignin and the fully oxypropylated derivative were quite close to those before the heat treatment.

Table 1. Thermal Stability Study of the Original Underivatized and Derivatized Lignins after Heating 20 °C above the Corresponding Glass Transition Temperatures (T_g) for 60 minutes

Sample / T_g (°C) / Heating temperature (°C)	$T_{1\%}$ (°C)			$T_{2\%}$ (°C)			$T_{5\%}$ (°C)		
	No heating	With heating	ΔT	No heating	With heating	ΔT	No heating	With heating	ΔT
Original kraft lignin / 153 / 173	176	215	29	195	230	35	235	256	19
Fully oxypropylated lignin / 128 / 148	191	219	28	220	240	20	255	277	18
Fully methylated lignin / 128 / 148	208	209	1	223	225	2	250	253	3

Since the overall data so far seems to implicate radical-induced coupling reactions derived from the phenolic OH groups within the original underivatized kraft lignin under thermal treatments (Fig. 1, 2, 3), such events, beyond a certain point, will manifest

themselves in complete sample insolubility (see discussion related to Fig. 2). Further-more, thermally stable carbon-carbon (C-C) biphenyl and/or carbon-oxygen biphenyl ether (C-O-C) linkages created during radical coupling reactions (Scheme 2B) will presumably require higher temperatures for certain levels of weight loss compared to its initial state. Therefore, the TGA method was used to qualitatively but indirectly determine the potential radical coupling reactions. The original kraft lignin and its derivatives were heated at 20 °C above their respective glass transition temperatures for 60 minutes under nitrogen. The samples were then cooled to room temperature before being re-weighed and subjected to a thermogravimetric analytical scan.

Table 1 shows that the original kraft lignin, upon being heated for one hour above its T_g, required temperature increases of 29, 35, and 19 °C to achieve 1%, 2%, and 5% weight losses, respectively (see ΔT data in Table 1). The fully oxypropylated kraft lignin also required increases of 28, 20, and 18 °C to achieve 1%, 2%, and 5% weight losses, respectively (see ΔT data in Table 1). Heating of the fully methylated kraft lignin at 20 °C above its T_g, however, showed only 1 to 3 °C differences in the ΔT data reported in Table 1.

Additional supporting evidence for the onset of thermally induced coupling reactions within kraft lignin was also obtained from DSC analyses, which were used to determine the T_g of the original, fully oxypropylated, and methylated derivatives after being heated at 20 °C above their T_g for 60 minutes.

Significant T_g increases for the original and oxypropylated kraft lignins were apparent (Fig. 4).
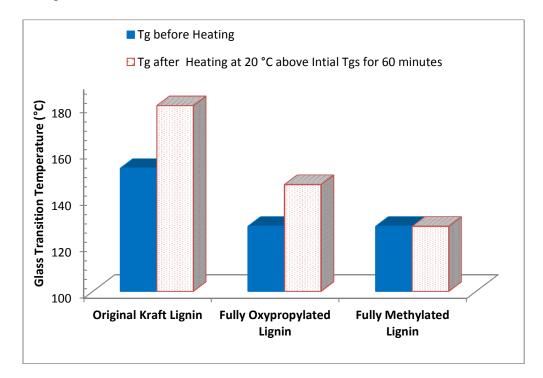

Fig. 4. Glass Transition temperatures of the original underivatized, fully oxypropylated and fully methylated lignins before and after heating 20 °C above their initial glass transition temperatures. Significant increases are observed in the T_gs of the original underivatized and oxypropylated lignins while there is no increase in the T_g of the methylated derivative.

More specifically, the T_g of the original kraft lignin increased by 27 °C and that of the fully oxypropylated derivative by 18 °C. The observed increases in the T_g can be rationalized on the basis of thermally induced coupling reactions within these two samples as already manifested by the observed increases in their molecular weights and the breadth of molecular weight distribution (Fig. 2) (Claudy *et al.* 1983).

Effect of Heating on the Molecular Weight Characteristics of the Original Underivatized and Derivatized Kraft Lignins

The effect of various thermal treatments on the molecular weight distributions of the original underivatized kraft lignin and its derivatives, when heated at 20 °C above their glass transition temperatures (Fig. 5A), were evaluated using GPC analyses.
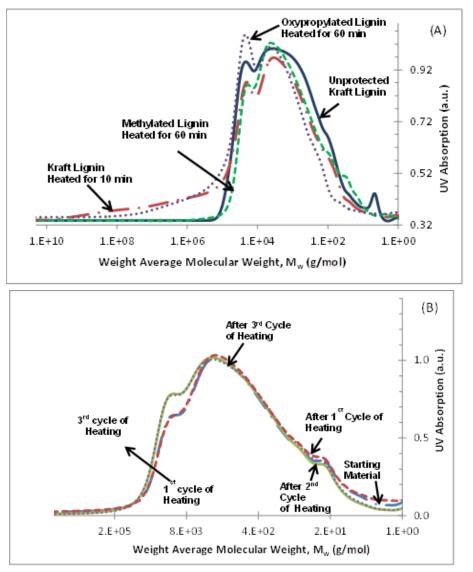

Fig. 5. (A) Effect of heating on the molecular weight distribution of the original underivatized and derivatized lignins. The molecular weight of the original underivatized lignin and of fully oxypropylated lignin is seen to significantly increase while the molecular weight of fully methylated lignin remains stable; (B) Effect of melting and cooling cycles on the molecular weight distribution of fully methylated lignin. Only minor changes in the molecular weight distribution were observed after three consecutive hourly cycles of heating (20 °C above its Tg) and cooling.

Since the original underivatized kraft lignin was prone to form insoluble materials, it was heated for only 10 minutes, while its derivatives were heated for 60 minutes.

Some moderate variations in the modality of the gel permeation chromatograms were apparent and most likely caused by different degrees of physical association between individual molecular species (Contreras *et al.* 2008; Guerra *et al.* 2007; Sarkanen *et al.* 1982; Sarkanen *et al.* 1984). However, an extreme broad tailing appeared after the thermal treatments in the higher molecular weight region for both the original underivatized kraft lignin and the fully oxypropylated derivative. It should be mentioned that this is not unusual in the context of molecular weight changes occurring within branched polymeric systems. Cross-coupling of branched and highly functional molecular species typically leads to a highly polydisperse behavior, manifested in the observed tailing (Argyropoulos *et al.* 1987a,b,c). In contrast, the fully methylated kraft lignin (>99%) showed no such tailing, exhibiting a molecular weight profile nearly identical to the original kraft lignin.

The consistently stable thermal behavior of the kraft lignin whose phenolic hydroxyl groups were fully methylated paved the way in posing the question: would this material be stable if repeatedly subjected to heating and cooling cycles? Consequently, a fully methylated lignin sample was subjected to multiple heating and cooling cycles to simulate actual thermal processing conditions. The sample was heated at 148 °C (20 °C above its T_g) and isothermally conditioned at this temperature for 60 minutes followed by cooling to room temperature. This heating and cooling cycle was repeated three times. After each cycle, a small portion of the treated sample was removed for a GPC analysis (Fig. 5B).

As a result, the molecular weight characteristics of all samplings remained nearly identical without a high molecular weight tailing effect. The M_w increased from 7,900 g/mol to about 11,000 g/mol, due to a minor change in the molecular weight distribution, which is most likely caused by thermally induced variations in the lignin's physical associative interactions.

The Benefits of Phenolic Hydroxyl Derivatization on Lowering the Glass Transition Temperature of Softwood Kraft Lignin

Earlier reports on lignin derivatives have shown that as the degree of derivatization increases, the T_g of the derivatives is monotonically reduced (Glasser *et al.* 1986; Kelley *et al.* 1988; Lisperguer *et al.* 2009). This is to be expected, since such derivatizations interfere with the hydrogen bonding patterns in these materials. Such substituents, depending on their structure, may also increase the free volume of the polymer system with a concomitant reduction in the T_g. In this respect, oxypropylation is more effective at reducing the lignin's T_g than methylation. However, methylation of the phenolic OH groups can eliminate most of the hydrogen bonding interactions in the lignin, whereas the oxypropylation of phenolic OH groups will create an equal amount of aliphatic OH groups in the lignin. The observed progressive reductions of T_g upon increasing the level of derivatizations for both methylation and oxypropylation were therefore expected (Fig. 6). At the highest phenolic derivatization levels (>99%), both methylated and oxypropylated derivatives were found to have a T_g of 128 °C (Fig. 6). The hydrogen bonding interactions from the newly formed aliphatic OH groups in the oxypropylated kraft lignin likely counteract the T_g reduction caused from the free volume

effect. Overall, softwood kraft lignin is highly susceptible to thermally induced reactions that cause severe alteration of its polymer characteristics. These events seriously interfere with and prevent such materials from being considered candidates for thermoplastic applications. The relatively high T_g measured for an underivatized softwood kraft lignin (153 °C) implies that such temperatures need to be reached and exceeded in order to allow for possible melt flow to occur. Such elevated temperatures will unavoidably cause the onset of thermal events that lead to the formation of irreversible cross-linking and intractable materials with no thermoplastic processing possibilities. However, by progressively eliminating the phenolic OH groups from within the structure of softwood kraft lignin by methylation, the thermal stability of these materials is dramatically enhanced and T_g are also reduced, which in turn reduces the temperatures required for processing (Fig. 6).
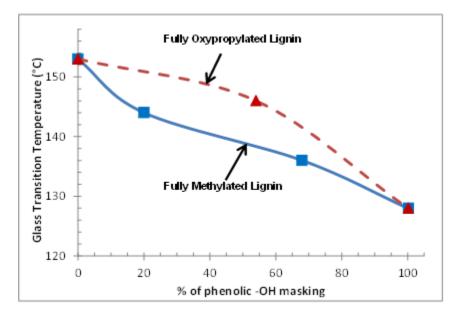

Fig. 6. Effect of derivatization level on glass transition Temperature (T_g). With increase of derivatization level (both for oxypropylation and methylation) glass transition temperature decreases

CONCLUSIONS

1. This work has attempted to provide a focused molecular understanding of the way the polymeric properties of kraft lignin and its derivatives are affected by thermal treatments.

2. Radical coupling mechanisms offer a sound basis for an explanation of the thermal behavior of softwood kraft lignin. Phenoxy radicals and their derived quinone methide intermediates have been used to explain the observations.

3. Overall, the selective masking of the phenolic hydroxyl groups by oxypropylation and methylation was anticipated to promote significant thermal stabilization of softwood kraft lignin. The fully methylated derivative was found to have excellent thermal stability, even when subjected to repeated heating and cooling cycles for up to 3

hours. However, the fully oxypropyled derivative showed less thermal stability than its fully methylated counterpart. This is likely to be caused by a dehydration mechanism of the secondary hydroxyls present on the mono-oxypropyl substituents of the kraft lignin derivative.

REFERENCES

Amen-Chen, C., Pakdel, H., and Roy, C. (2001). "Production of monomeric phenols by thermochemical conversion of biomass: A review," *Bioresource Technology* 79(3), 277-299.

Antal, M. J., Jr. . (1985). "Biomass pyrolysis: A review of the literature.," *Advances in Solar Energy*, *Vol. 2*, K. W. Boer, and J. A. Duffie (eds.), ASES Publication, Boulder, USA, 175-255.

Argyropoulos, D. S. (1995). "^{31}P NMR in wood chemistry: A review of recent progress," *Research on Chemical Intermediates*, 21(3), 373-395.

Argyropoulos, D. S. (2012). "High value lignin derivatives, polymers & copolymers & use thereof in thermoplastic, thermoset and composite applications," US Patent Application No. 61/601,181, February 21, 2012.

Argyropoulos, D. S. (1994). "Quantitative phosphorus-31 NMR analysis of lignins, a new tool for the lignin chemist," *Journal of Wood Chemistry and Technology* 14(1), 45-63.

Argyropoulos, D. S., Berry, R. M., and Bolker, H. I. (1987a). "Polymerization beyond the gel point, 2. A study of the soluble fraction as a function of the extent of reaction," *Die Makromolekulare Chemie* 188(8), 1985-1992.

Argyropoulos, D. S., Berry, R. M., and Bolker, H. I. (1987b). "Polymerization beyond the gel point. I. The molecular weight of sol as a function of the extent of reaction," *Journal of Polymer Science Part B: Polymer Physics* 25(6), 1191-1202.

Argyropoulos, D. S., Berry, R. M., and Bolker, H. I. (1987c). "Species distribution within the soluble phase beyond the gel point," *Macromolecules* 20(2), 357-361.

Asikkala, J., Tamminem, T., and Argyropoulos, D. S. (2012). "Accurate and reproducible determination of lignin molar mass by acetobromination," *Journal of Agricultural and Food Chemistry*, 60(36), 8968-8973.

Boerjan, W., Ralph, J., and Baucher, M. (2003). "Lignin biosynthesis," *Annual Review of Plant Biology*, 54(1), 519-546.

Bonawitz, N. D. (2010). "The genetics of lignin biosynthesis: Connecting genotype to phenotype," *Annual Review of Genetics*, 44(1), 337-363.

Bozell, J. J., Holladay, J. E., Johnson, D., and White, J. F. (2007). "Top value added chemicals from biomass, Volume II: Results of screening for potential candidates from biorefinery lignin," *US Department of Energy Tech. Rep. PNNL-16983*, Pacific Northwest National Laboratory and National Renewable Energy Laboratory. Office of Scientific and Technical Information, Oak Ridge, TN.

Brebu, M., and Vasile, C. (2010). "Thermal degradation of lignin - A review," *Cellulose Chemistry and Technology* 44(9), 353-363.

Chandra, A., and Uchimaru, T. (2002). "The O-H bond dissociation energies of substituted phenols and proton affinities of substituted phenoxide ions: A DFT study," *International Journal of Molecular Sciences*, 3(4), 407-422.

Claudy, P., Létoffé, J. M., Camberlain, Y., and Pascault, J. P. (1983). "Glass transition of polystyrene versus molecular weight," *Polymer Bulletin* 9(4), 208-215.

Contreras, S. a., Gaspar, A. R., Guerra, A., Lucia, L. A., and Argyropoulos, D. S. (2008). "Propensity of lignin to associate: Light scattering photometry study with native lignins," *Biomacromolecules* 9(12), 3362-3369.

Crestini, C., Melone, F., Sette, M., and Saladino, R. (2011). "Milled wood lignin: A linear oligomer," *Biomacromolecules* 12(11), 3928-3935.

Danielson, B., and Simonson, R. (1998). "Kraft lignin in phenol formaldehyde resin. Part 1. Partial replacement of phenol by kraft lignin in phenol formaldehyde adhesives for plywood," *Journal of Adhesion Science and Technology* 12(9), 923-939.

Doherty, W. O. S., Mousavioun, P., and Fellows, C. M. (2011). "Value-adding to cellulosic ethanol: Lignin polymers," *Industrial Crops and Products* 33(2), 259-276.

Domburg, G. E., Rossinskaya, G., and Sergeeva, V. N. (1974). "Study of thermal stability of β-ether bonds in lignins and its models," *Thermal Analysis*, *Vol. 2*, H. G. Wiedemann (eds.), Birkhauser, Basel, Switzerland, 211-220.

Evans, R. J., Milne, T. A., and Soltys, M. N. (1986). "Direct mass-spectrometric studies of the pyrolysis of carbonaceous fuels: III. Primary pyrolysis of lignin," *Journal of Analytical and Applied Pyrolysis* 9(3), 207-236 and references therein.

Fengel, D., and Wegener, G. (1984). *Wood: Chemistry, Ultrastructure, Reactions*, W. de Gruyter, Berlin, New York.

Fenner, R. A., and Lephardt, J. O. (1981). "Examination of the thermal decomposition of kraft pine lignin by Fourier transform infrared evolved gas analysis," *Journal of Agricultural and Food Chemistry* 29(4), 846-849.

Froass, P. M., Ragauskas, A. J., and Jiang, J.-e. (1996). "Chemical structure of residual lignin from kraft pulp," *Journal of Wood Chemistry and Technology* 16(4), 347-365.

George, A. O., and Prakash, G. K. S. (2004). *Carbocation Chemistry*, John Wiley & Sons, Inc. New Jersey.

Gierer, J. (1980). "Chemical aspects of kraft pulping," *Wood Science and Technology* 14(4), 241-266.

Gierer, J., and Pettersson, I. (1977). "Studies on the condensation of lignins in alkaline media. Part II. The formation of stilbene and arylcoumaran structures through neighbouring group participation reactions," *Canadian Journal of Chemistry* 55(4), 593-599.

Glasser, W. G., Kelley, S. S., Rials, T. G., and Ciemniecki, S. L. (1986). "Structure property relationship of engineering plastics from lignin," *1986 Research and Development Conference, TAPPI*, pp. 157-161.

Glasser, W. G., Knudsen, J. S., and Chang, C.-S. (1988). "Multiphase materials with lignin. III. Polyblends with ethylene-vinyl acetate copolymers," *Journal of Wood Chemistry and Technology* 8(2), 221-234.

Gosselink, R. J. A., Abächerli, A., Semke, H., Malherbe, R., Käuper, P., Nadif, A., and van Dam, J. E. G. (2004). "Analytical protocols for characterisation of sulphur-free lignin," *Industrial Crops and Products* 19(3), 271-281.

Granata, A., and Argyropoulos, D. S. (1995). "2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxapholane, a reagent for the accurate determination of the uncondensed and condensed phenolic moieties in lignins," *Journal of Agricultural and Food Chemistry* 43(6), 1538-1544.

bioresources.com

Guerra, A., Gaspar, A. R., Contreras, S., Lucia, L. A., Crestini, C., and Argyropoulos, D. S. (2007). "On the propensity of lignin to associate: A size exclusion chromatography study with lignin derivatives isolated from different plant species," *Phytochemistry* 68(20), 2570-2583.

Hatakeyama, T., and Hatakeyama, H. (2010). *Thermal Properties of Green Polymers and Bio composites*, Kluwer Academic Publishers, Dordrecht, The Netherlands.

Hodge, I. M. (1994). "Enthalpy relaxation and recovery in amorphous materials," *Journal of Non-Crystalline Solids* 169(3), 211-266.

Jain, R. K., and Glasser, W. G. (1993). "Lignin derivatives. II. Functional ethers," *Holzforschung* 47(4), 325-332.

Jiang, J., and Argyropoulos, D. S. (1999). "Isolation and characterization of residual lignin in kraft pulp," *Journal of Pulp and Paper Science* 25(1), 25-29.

Jiang, Z., and Argyropoulos, D. S. (1994). "The stereoselective degradation of arylglycerol-beta-aryl ethers during kraft pulping," *Journal of Pulp and Paper Science* 20(7), J183-J188.

Kadla, J. F., and Kubo, S. (2003). "Miscibility and hydrogen bonding in blends of poly(ethylene oxide) and kraft lignin," *Macromolecules* 36(20), 7803-7811.

Kadla, J. F., Kubo, S., Venditti, R. A., Gilbert, R. D., Compere, A. L., and Griffith, W. (2002). "Lignin-based carbon fibers for composite fiber applications," *Carbon* 40(15), 2913-2920.

Kawamoto, H., Horigoshi, S., and Saka, S. (2007a). "Effects of side-chain hydroxyl groups on pyrolytic β -ether cleavage of phenolic lignin model dimer," *Journal of Wood Science* 53(3), 268-271.

Kawamoto, H., Horigoshi, S., and Saka, S. (2007b). "Pyrolysis reactions of various lignin model dimers," *Journal of Wood Science* 53(2), 168-174.

Kawamoto, H., Nakamura, T., and Saka, S. (2008a). "Pyrolytic cleavage mechanisms of lignin-ether linkages: A study on p-substituted dimers and trimers," *Holzforschung* 62(1), 50.

Kawamoto, H., Ryoritani, M., and Saka, S. (2008b). "Different pyrolytic cleavage mechanisms of β-ether bond depending on the side-chain structure of lignin dimers," *Journal of Analytical and Applied Pyrolysis* 81(1), 88-94.

Kawamoto, H., and Saka, S. (2007). "Role of side-chain hydroxyl groups in pyrolytic reaction of phenolic β-ether type of lignin dimer," *Journal of Wood Chemistry and Technology* 27(2), 113-120.

Kelley, S. S., Glasser, W. G., and Ward, T. C. (1988). "Engineering plastics from lignin XIV. Characterization of chain-extended hydroxypropyl lignins," *Journal of Wood Chemistry and Technology* 8(3), 341-359.

Kramer, K. J., Manaset, E., and Worrell, E. (2010). "Energy efficiency opportunities in the U.S. pulp and paper industry," *Energy Engineering* 107(1), 21-50.

Kubo, S., and Kadla, J. F. (2005). "Kraft lignin/poly(ethylene oxide) blends: Effect of lignin structure on miscibility and hydrogen bonding," *Journal of Applied Polymer Science* 98(3), 1437-1444.

Li, Y., Mlynár, J., and Sarkanen, S. (1997). "The first 85% kraft lignin-based thermoplastics," *Journal of Polymer Science Part B: Polymer Physics* 35(12), 1899-1910.

Li, Y., and Sarkanen, S. (1999). "Thermoplastics with very high lignin contents," *Lignin: Historical, Biological, and Materials Perspectives*, *Vol. 742*, American Chemical Society, 351-366.

Liitiä, T. M., Maunu, S. L., Hortling, B., Toikka, M., and Kilpeläinen, I. (2003). "Analysis of technical lignins by two- and three-dimensional NMR Spectroscopy," *Journal of Agricultural and Food Chemistry* 51(8), 2136-2143.

Lisperguer, J., Perez, P., and Urizar, S. (2009). "Structure and thermal properties of lignins: characterization by infrared spectroscopy and differential scanning calorimetry," *Journal of the Chilean Chemical Society* 54, 460-463.

Marton, J. (1971). *Lignin: Occurrence, Formation, Structure, and Reactions*. Wiley-Interscience, New York, USA.

Mathers, R. T. (2012). "How well can renewable resources mimic commodity monomers and polymers?," *Journal of Polymer Science Part A: Polymer Chemistry* 50(1), 1-15.

Nadji, H., Bruzzèse, C., Belgacem, M. N., Benaboura, A., and Gandini, A. (2005). "Oxypropylation of lignins and preparation of rigid polyurethane foams from the ensuing polyols," *Macromolecular Materials and Engineering* 290(10), 1009-1016.

Nakamura, T., Kawamoto, H., and Saka, S. (2007). "Condensation reactions of some lignin related compounds at relatively low pyrolysis temperature," *Journal of Wood Chemistry and Technology* 27(2), 121-133.

O'Neill, M. J. (1964). "The analysis of a temperature-controlled scanning calorimeter," *Analytical Chemistry* 36(7), 1238-1245.

Ohashi, Y., Uno, Y., Amirta, R., Watanabe, T., Honda, Y., and Watanabe, T. (2011). "Alkoxyl- and carbon-centered radicals as primary agents for degrading non-phenolic lignin-substructure model compounds," *Organic & Biomolecular Chemistry* 9(7), 2481-2491.

Petrie, S. E. B. (1972). "Thermal behavior of annealed organic glasses," *Journal of Polymer Science Part A-2: Polymer Physics* 10(7), 1255-1272.

Rex, R. W. (1960). "Electron paramagnetic resonance studies of stable free radicals in lignins and humic acids," *Nature* 188(4757), 1185-1186.

Rials, T. G., and Glasser, W. G. (1984). "Engineering plastics from lignin. X. Enthalpy relaxation of prepolymers," *Journal of Wood Chemistry and Technology* 4(3), 331-345.

Roberts, V. M., Stein, V., Reiner, T., Lemonidou , A., Li, X., and Lercher, J. A. (2011). "Towards quantitative catalytic lignin depolymerization," *Chemistry – A European Journal* 17(21), 5939-5948.

Sadeghifar, H., Cui, C., and Argyropoulos, D. S. (2012). "Toward thermoplastic lignin polymers. Part 1. Selective masking of phenolic hydroxyl groups in kraft lignins via methylation and oxypropylation chemistries," *Industrial & Engineering Chemistry Research, DOI: 10.1021/ie301848j.*

Sarkanen, S., Teller, D. C., Abramowski, E., and McCarthy, J. L. (1982). "Lignin. 19. Kraft lignin component conformation and associated complex configuration in aqueous alkaline solution," *Macromolecules* 15(4), 1098-1104.

Sarkanen, S., Teller, D. C., Stevens, C. R., and McCarthy, J. L. (1984). "Lignin. 20. Associative interactions between kraft lignin components," *Macromolecules* 17(12), 2588-2597.

Sazanov, Y., and Gribanov, A. (2010). "Thermochemistry of lignin," *Russian Journal of Applied Chemistry* 83(2), 175-194.

Sette, M., Wechselberger, R., and Crestini, C. (2011). "Elucidation of lignin structure by quantitative 2D NMR," *Chemistry – A European Journal*, 17(34), 9529-9535.

Steelink, C. (1966). "Stable free radicals in lignin and lignin oxidation products," *Lignin Structure and Reactions*, *Vol. 59*, J. Marton (eds.), American Chemical Society, Washington, DC, USA, 51-64.

Vollhardt, K. P. C., and Schore, N. E. (2007). *Organic Chemistry: Structure and Function*. Susan Finnemore Brennan, Craig Bleyer, New York, USA.

Wu, L. C. F., and Glasser, W. G. (1984). "Engineering plastics from lignin. I. Synthesis of hydroxypropyl lignin," *Journal of Applied Polymer Science* 29(4), 1111-1123.